CAMELS-Chem: Augmenting CAMELS (Catchment Attributes and Meteorology for Large-sample Studies) with Atmospheric and Stream Water Chemistry Data

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Abstract. Large sample datasets are transforming hypothesis testing and model fidelity in the catchment sciences, but few large stream water chemistry datasets exist with complementary streamflow, meteorology, and catchment physiographic attributes. The existing CAMELS (Catchment Attributes and Meteorology for Large-sample Studies) dataset includes data on topography, climate, streamflow, land cover, soil, and geology across the continental U.S. With CAMELS-chem, we pair ~~Here, we~~ these existing catchment attribute data with atmospheric deposition data from the National Atmospheric Deposition Program and ~~pair atmospheric deposition and water chemistry related information with the existing CAMELS (Catchment Attributes and Meteorology for Large-sample Studies) dataset,~~ which ~~which~~ . ~~The newly developed dataset, CAMELS-Chem, comprises U.S. Geological Survey~~ water chemistry data and instantaneous discharge from U.S. Geological Survey over the period from 1980 through 2018. ~~in 506 minimally impacted headwater catchments.~~ The CAMELS-Chem dataset includes 18 common stream water chemistry constituents: Al, Ca, Cl, Dissolved Organic Carbon, Total Organic Carbon, HCO_3~~HCO_3~~, K, Mg, Na, Total Dissolved Nitrogen [nitrate + nitrite + ammonia + organic-N], Total Organic Nitrogen, NO_3~~NO_3~~, Dissolved Oxygen, pH (field and lab), Si, SO_4, and water temperature for up to 516 minimally impacted headwater catchments. ~~We also provide an a~~Annual ~~wet~~ deposition loads and concentrations include ~~from the National Atmospheric Deposition Program over~~

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~~the same catchments that includes:~~ Ca, Cl, H, K, Mg, Na, NH₄, NO₃, SO₄. and Total Nitrogen from deposition [precipitation NO_3~~NO3~~ + NH_4~~NH4~~, dry deposition of particulate NH_4~~NH₄~~, + NO_3~~NO3~~, and gaseous NH_3~~NH₃~~]. We pair ~~d~~ mean daily discharge measurements for all chemistry samples and instantaneous discharge for about 30%. We demonstrate the geographic and hydroclimatic coverage of the dataset and explore the consistency of sampling across sites, seasons, and discharge. ~~of~~Further, t~~T~~o motivate ~~wider~~ use by ~~the larger~~the larger scientific community across a variety of disciplines, we exemplify the potential use of this dataset for ~~develop three example~~ two analyses: 1. Atmospheric-aquatic linkages using atmospheric and stream SO_4~~SO₄~~ trends, and 2. Geological-biogeochemical linkages using weathering relations.

1 Introduction

Earth surface processes include coupled and complex processes that involve atmosphere, biosphere, lithosphere and hydrosphere, however, tracking these important processes across time, space and disciplines remains a challenge that is, amongst others, related to data availability and connectedness. To address the need for 'balancing breadth with depth' (Gupta et al., 2014, Hubbard et al., 2020), the hydrological sciences have developed large sample size datasets that are of high quality and then made these available to the research community. One of the key advantages of aggregating and harmonizing data into larger sample size datasets is to test how model hypotheses reproduce observed behaviour across variable conditions and sites to reduce the uniqueness of place issues (i.e. individual catchment behavior might not be generalizable to explain a larger scale pattern and vice versa) (Gupta et al., 2014) (Hubbard et al., 2020). As a result, several recent efforts have focused on generating and using datasets across the continental U.S. (CONUS) where observation networks are relatively dense. For example, the Model Parameter Estimation Experiment (MOPEX, Duan et al., 2006) dataset has been used to detect the effects of shifts from snow to rain on streamflow (Berghuijs et al. 2014) and to better diagnose the cause of catchment-scale water budgets (Brooks et al., 2015). Recent efforts have extended the record and detail of auxiliary data of older efforts (e.g. MOPEX) to develop longer-term streamflow and hydrometeorological forcing data for a larger number of minimally disturbed catchments, including the continental U.S (Newman et al. 2014), Chile (Alvarez-Garreton et al., 2018), and Brazil (Chagas et al., 2020). The Global River Water Quality archive (GRQA) and GLObal RIver Chemistry Database (GLORICH) have offered opportunities for water quality analyses across time and land scale (Hartmann et al. 2014, Virro et al. 2021) and the Catchment Attributes for Large-Sample Studies (CAMELS, Newman et al. (2015)) compile high quality streamflow measurement in 671 unimpaired catchments across the CONUS, as well as climate forcing datasets (e.g. daily precipitation and temperature) and physiographic properties (e.g. land cover, topography, etc., Addor et al. (2017). CAMELS has seen widespread adoption by the hydrological community as a benchmarking tool for hydrological models (Melsen et al. 2018, Mizukami et al. 2019, Pool et al. 2019), in the development of hydrological signatures and new information theory-based approaches, and the application of novel machine learning tools (Kratzert et al. 2019). The combination of catchment attributes and matching datasets on stream water chemistry has recently been developed for Germany (Ebeling et al. 2022), however, for the CONUS this approach

has not seen as much development (Arora et al. 2023). Furthermore, atmospheric deposition data is typically not included in such data sets, despite the significant impact of atmospheric contribution to stream chemistry.

Many important insights across Earth science disciplines over the last several decades derived from investigations that combined several datasets such as long-term stream chemistry data, stream discharge, hydroclimatology, and catchment properties (e.g. vegetation, geology, topography). For example, global analyses of CO_2 evasion from headwater streams have helped to quantify global fluxes (Gaillardet et al., 2018; Horgby et al., 2019; Lauerwald et al., 2015; Raymond et al., 2013). Changes in dissolved organic carbon (DOC) in stream water were partially related to changes in atmospheric deposition and acidity only viewable with longer records (Monteith et al., 2007). Stream flow and chemistry data, in particular pairedcombined(?) concentration and discharge data, have also been shown to illuminate subsurface flow paths and chemical vertical stratification (Stewart et al., 2022; Zhi and Li, 2020). Applying an integrative dataset in the Northeastern U.S., a recent study showed differential sensitivity of headwater catchments to reductions in SO_4 and NO_3 and resulting variations in stream DOC efflux (CITE Adler et al. 2021). Importantly, this study confirmed that much of the long-term recovery from acid rain is mediated by catchment-scale processes in variable soils and bedrock as well as variable hydrological and climatic forcings. Only by aggregating data across many catchments could these interacting factors affecting stream chemistry be deterimineddetermined because transferability from a small number of regional catchments is very limited (Clow et al, 1999; Garmo et al., 2014; Harpold et al., 2010). Further, long-term water chemistry datasets have also given insight into rock weathering and solute flux estimates. For example, Godsey et al. (2009) used theeh GLORICH dataset that focuses on large, human impacted riverine systems and contains corresponding catchment properties and streamflow data and showed the ubiquity of 'chemostasis, i.e. solute fluxes being primarily driven by stream discharge and not variations in concentrations in many catchments. More recent work using 2,186 catchments from the Global River Chemistry Dataset (GLORICH) began to illustrate the role of aridity and catchment properties in controlling the concentration-discharge (C-Q) relationship in key solutes (Godsey et al., 2019).

Thus, we now have There are opportunities to inform our understanding of the inter-relationships between water chemistry, hydrology, and biogeochemistry by developing facilitated by datasets that link stream chemistry to discharge and other catchment properties. For example, Vlah et al. (2023), have combined data from watershed studies and supplemented these with watershed attributes. Our contribution is the compilation of a new dataset that takes advantage of one of the most comprehensive collections of catchment attributes across the CONUS i.e., CAMELS (Addor et al., 2017; Newman et al., 2014). Building on CAMELS, we developed "CAMELS-Chem", a relational database that provides fast query processing, enforces data integrity, provides detailed information about current data and schema (i.e., relational structure), and represents a flexible platform to export data in a consistent format for external analysis. The database comprises

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individual water chemistry measurements harvested from the U.S. Geological Survey (USGS) National Water Information System (NWIS), with up to 516 catchments and 18 constituents (USGS 2023) and earliest atmospheric deposition data from the National Atmospheric Deposition Program (NADP, available since 1985). While stream data from as early as 1898 is available for some instances (and is included in the relational database), this publication and accompanying dataset covers the timeframe from 1980 to 2018 because CAMELS spans the timeframe from 1980 to 2014. We first introduce the methods used to develop the CAMELS-Chem database and dataset (Section 2) and then summarize the availability and spatial patterns of key water chemistry constituents (Section 3). Finally, we exemplify the utility of CAMELS-Chem for interdisciplinary applications that require several data streams for (bio)geo-chemistry, ecology, and hydrology (Section 4). These examples can help illuminate how the dataset can be used and therefore facilitate the integration of ideas, as it is often challenging to see connections across disciplinary boundaries. Readers are also referred to cross-disciplinary publications already using this dataset (Zhi et al. 2019, Zhi and Li 2020, Adler et al. 2021, Zhi et al. 2021, Li et al. 2022, Underwood et al. 2023).

2 Materials and Methods

2.1 Data sources and description 2.1 Data Harvesting and Integration Approach Data Sources

 2.1 Data sources and description

CAMELS covers the time period from 1980-2014 and we added stream discharge and solute concentration for the entire length of record (as early as 1898) until 2018. To showcase data for the timeframe where both CAMELS data and stream data are available, all figures in the main body of the publication feature the stream data starting in 1980. We show data for the entire length of record in supplementary materials.

CAMELS-Chem record shows that most of its sites are drawn come from the USGS Hydrologic Benchmark Network (https://www.usgs.gov/centers/new-york-water-science-center/science/hydrologic-benchmark-network) that have been utilized in previous studies (Godsey et al. 2019) and are supplemented with all additional shorter or less consistent USGS NWIS records from the Hydro-Climatic Data Network (https://water.usgs.gov/GIS/metadata/usgswrd/XML/hcdn.xml).

The USGS provides a consistent methodology, locations, and paired discharge record for all collected water samples. Approximately 93% of the samples in CAMELS-Chem have a paired daily discharge value; however, the coverage for paired instantaneous discharge values was lower (~15%) because not all gauges provide hourly observations or they provide discharge only from a more recent part of the record. For these cases the (bio)geo-chemical sample time was adjusted forward/backward to pair with the closest quarter -hour (or sometimes hourly) instantaneous discharge observation. Missing time stamps for (bio)geo-chemical sampling is more challenging to correct. We address this by making the assumption that field technicians

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generally collect samples for multiple solutes at the same time, thus the recorded timestamp for one solute can be applied to all taken on that day. By assuming one sampling time every day per site we obtained 397 more instantaneous discharge values (out of a total of 8,975 records without timestamps). Using hourly observations and field observations during water chemistry sampling, we provide instantaneous data from roughly 30% of samples.

2.2 Data Harvesting and Integration Approach

Integrating water resources data from multiple sources can be a process replete with challenges including missing data, mis-matched sample times, inconsistent parameter names, or varying units of measure (Sprague et al. 2017, Niu et al. 2018). While NWIS sources already have high quality records that have been quality-assured and normalized, issues of missing data and different constituent names across catchments can present problems for data harmonization and integration. To address these challenges, we used state-of-the-art methods to automate data acquisition and integration, coupled with a relational database (Bansal and Kagemann 2015). The Extract, Transform, and Load (ETL; Figure S1 in supplementary materials) framework from Pentaho Data Integration was employed to: (1) extract discharge and water quality data from siloed systems; (2) transform the data into formats to fit operational needs; and (3) load the data into a relational database to provide maximum flexibility for retrieval, exploration and analysis.

During extraction, we relied on unique gauge identifiers from NWIS to relate the two gage-specific data sources: 1) instantaneous and daily mean discharge data and 2) (bio)geo-chemical stream water quality data. Of the original 671 CAMELS watersheds, 506 watersheds returned instantaneous or daily mean discharge data and 488 returned both discharge and water quality data for the time between 1980 and 2018. The transformation part of the workflow addressed data quality issues and harmonization before data were uploaded to the repository. For example, we normalized differing units of measure across constituents and sample times across time zones. We employed algorithms to impute missing time stamps for a subset of the water quality records (see Data Sources and Description section). For the final comprehensive data repository, we selected Oracle's free and open-source database (PostgreSQL 2020). A relational database provides fast query processing, enforces data integrity, provides detailed information about current data and schema (i.e., relational structure), and represents a flexible platform to export data in a consistent format for external analysis. Statistics were calculated for key parameters such as probability of exceedance, standard deviation, low/medium/high flow conditions, mean daily and annual flow. These statistics appear in the following figures and are also available as part of this data release.

3 Results

3.1 Stream Water Chemistry

The CAMELS-Chem dataset comprises 18 water chemistry and property values (Table 1) and is summarized for general water quality parameters (discharge, dissolved oxygen, pH, and temperature), carbon and nutrient species ((DOC), total organic

carbon (TOC), dissolved organic nitrogen (DON), total organic nitrogen (TON), total dissolved nitrogen (TDN), nitrate (NO_3)), anions (Cl, bicarbonate (HCO_3), sulfate (SO_4) and cations (Ca, K, Mg, Na, Si, and Al, Figure 1). While the lengths of discharge and climate records extend up to or greater than 30 years for many CAMELS-Chem catchments, the water chemistry data are not as continuous and spatially consistent (Figure 1 for all flows and 2 for flow duration curve [FDC]>66%). The total number of stream water samples varies substantially depending on the variable of interest, which should be taken into consideration when using this dataset. For example, the dataset has 34,704 total Si measurements from 325,477 catchments, compared to only 11,101 DOC measurements from 17,989 catchments (Figure 1r and 1e, respectively).

Table 1: The stream water chemistry datasets in the CAMELS-Chem dataset including attribute, name, abbreviation in the database, description, units and USGS parameter codes.

Attribute	Name	Database abbreviation	Description	Units	USGS parameter code(s)
Q	discharge		discharge		
DO	Dissolved Oxygen	o	Water, unfiltered	mg/l	300
pH	pH	ph	Water, unfiltered, field	std units	400
pH_1	pH	ph2	Water, unfiltered, laboratory	std units	403
temp	water temperature	temp	Water, field	degree C	10
DOC	Dissolved Organic Carbon	doc	Water, filtered	mg/l	681
TOC	Total Organic Carbon	toc	Water, unfiltered	mg/l	680
DON	Dissolved Organic Nitrogen	don	Water, filtered	mg/l	607
TON	Total Organic Nitrogen	ton	Water, unfiltered	mg/l	605
TDN	Total Dissolved Nitrogen	tn	Water, filtered [nitrate + nitrite + ammonia + organic-N]	mg/l	602
NO_3	Nitrate	no3	Water, filtered and total	mg/l as N	618, 620
Cl	Chloride	cl	Water, filtered and total	mg/l	940, 99220
HCO_3	Bicarbonate	hco3	Water, filtered, field, inflection-point (incremental titration method)	mg/l	453
SO_4	Sulfate	so4	Water, filtered and total	mg/l	945, 946, 99127
Ca	Calcium	ca	Water, filtered	mg/l	915
K	Potassium	k	Water, filtered	mg/l	935
Mg	Magnesium	mg	Suspended sediment, total	mg/l	925
Na	Sodium	na	Water, filtered	mg/l	930

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| Si | Silica | si | Water, filtered | mg/l | 955 |
| Al | Aluminium | al | Water, filtered | µg/l | 1106 |

3.1 Water Chemistry Constituents and Data Availability and Patterns in Water and Deposition Chemistry

~~While the lengths of discharge and climate records extend up to or greater than 30 years for many CAMELS-Chem catchments, the water chemistry data are not as continuous and spatially consistent (Figure 2 and S1 for the entire length of record). The total number of stream water samples varies substantially depending on the variable of interest, which should be taken into consideration when using this dataset. For example, the dataset has 34,704 total Si measurements from 325477 catchments, compared to only 11,101 DOC measurements from 17989 catchments (Figure 2r and 2e, respectively). In general, weathering-related solutes (Si, Ca, K, Mg, Na) are more comprehensively sampled (i.e. longer records and more catchments) than biologically driven constituents (NO3, TDN, DOC). Temperature and DO are sampled more often because they are part of the standard USGS field measurements at the time of water chemistry sampling. Annual average atmospheric deposition maps developed by the National Atmospheric Deposition Program (NADP) are reported for each catchment (Figure 4).~~

Patterns of different water chemistry constituents reflect the broad range of geology, climate, land use history, land cover and other factors (Figure 1 and 2). For example, water temperature shows clear latitudinal patterns in both mean and coefficient of variation (CV, Figure 1, 2d) that likely reflect warmer climate and greater solar radiation in southern locations. Conversely, variables like DO and pH have much smaller variability in mean and CV and less geographic patterning (Figure 1, 2b and c, respectively). Some of the biologically derived solutes such as DOC and TOC show high variability in mean and CV across CONUS, without clear geographic patterns (Figure 1, 2e and f). In contrast, many of the nitrogen constituents show hot spots of agriculture in the Midwest and upper great plains (Figure 1,2g-j). Similarly, ions associated with agriculture and human impacts, like Ca, K, and Mg had higher mean values and larger CV in the central part of CONUS (Figure 1,2 n, k and p); whereas the geographical pattern of mean and variance of Si and Al is less distinct (Figure 1,2 r and s). These results shown here demonstrate the complexity of spatial patterns across the CONUS. In the following sections we offer more background on the strengths and weaknesses of the dataset for different applications.

3.2 Consistency of Stream Sampling Across Sites and Seasons

CAMELS-Chem offers long-term records for trend analysis and broad geographic coverage in catchments (Figure 3 as well as S4 in supplementary materials). Because USGS sampling foci varied between decades, temporal biases in the sampling record exist (Shanley et al. 2015). For example, many of the stream water constituents impacted by acid rain (i.e., SO_4 and Ca) were sampled less frequently starting in the late 1990's (Fig 3m and n). In contrast, sampling frequency for many solutes related to local water quality issues (i.e. NO_3, and K) have increased in recent decades (Figure 3j and o). The NO_3 data are more abundant in the Midwest and along the east coast where sampling for nutrients is common. In contrast, DOC observations

highlight the location of long-term sites focused on minimally human-impacted catchments (i.e., USGS Hydrologic Benchmark Network) that have the most comprehensive sampling of all solutes (Figure 3e).

Longer records and sampling across seasons increase the capability for trend detection. Field data collection is more consistently measuring water DO, pH and temperature (up to 516 out of the 671 CAMELS watersheds, Figure 3b-d). Temperature measurements demonstrate the dedication of USGS staff, with 3,000-7,000 samples taken each year, which led to >400 sites with >20 years of records and >100 samples (Figure 3d). In general, other chemical analyses are done with filtered samples (exception TON) back in a laboratory. Among these samples, weathering-related, lithogenic solutes such as Ca, K, Mg, Na and Si (Figure 3n-r) are more comprehensively sampled (i.e. longer records and more catchments) than biologically driven constituents such as DOC, TOC or organic nitrogen (Figure 3e-h). For example, lithogenic solutes have around 50 sites with >20 year records and >100 samples, with a total of between 50-150 catchments and 1,000-2,000 samples each year (Figure 4. In contrast, biologically related solutes are sampled around 500-1,000 times per year, have <50 records that are >20 years and >100 samples. NO_3 is sampled 1,000-2,000 times per year, but much of the additional sampling is concentrated in agricultural catchments in the midwestern part of the US. Thus, users of the data should be aware of the different sampling frequencies at each location, and while sampling frequency varies greatly by solute and water year, different seasons are roughly evenly represented in the dataset (Figure 4). Across all watersheds, CAMELS-Chem covers a wide range of hydroclimate that offers ample opportunities for investigating the connection between climate, catchment attributes and stream water chemistry. We illustrate this by showing the range of some variables from the CAMELS database (Figure 5) for all 671 catchments versus the catchments sampled by CAMELS-Chem for Cl (high sampled) and Al (less sampled). The range of catchments sampled is nearly identical between CAMELS and CAMEL-Chem, which both span a wide range of hydrological and hydrometerological conditions.

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3.3 Consistency of Sampling Across Discharge Records and Variable Hydroclimate

Because CAMELS-Chem is paired with measured discharge data, we can effectively assess and constrain the effects of discharge on water chemistry analyses. Concentration-discharge (C-Q) relationships are routinely used to compute solute loads for mass budgets (Cohn et al. 1989) and have been used to infer catchment effects on biogeochemical cycling (Basu et al. 2010, Musolff et al. 2015). CAMELS-Chem has distinct advantages in this context, as we used instantaneous (hourly) discharge data to supplement the NWIS database and 30-year daily discharge records are a reference for C-Q ranges. Because Q values are more likely to change over daily periods at high flows than low flows, instantaneous discharge measurements are more critical on high flow days than low flow days.

To apply a C-Q analyses to a dataset, the stream chemistry sampling for the solute of interest must span a large range of discharge values. Conversely, if only low flow (baseflow) values are available, careful subsampling is required. To aid assessment of the dataset in this context, we offer a visual representation of the coverage of the percent of the FDC (i.e. highest minus lowest percentiles of water sampling dates) for each catchment (Figure 6 and S5). The CAMELS-Chem sampling covers >75% of the FDC curve in most catchments, with coverage less than 50% of the FDC in parts of the Gulf Coast and Upper Midwest areas (Figure 6). Despite the greater sampling of the weathering related solutes (Figure 6m-q), all solutes show relatively high coverage of the FDC, including the biological solutes that were sampled many less times and over shorter records (e.g. Figure 6d-i). In terms of sampling consistency and numbers across the FDC, we look at the percent fraction of sampling occurs in each tercile of the FDC across solutes (Table 2), where even sampling would be 33% of samples in each tercile. There is a small bias to sampling at high flows (<33% tercile), especially for the biological solutes and many lithogenic solutes (Table 2).

Table 3X: The percentage of samples that were sampled at flows with exceedance probabilities on the flow duration curve (FDC) < 33% (higher flows) and >66% (lower flows) for water years 1980-2018. pH here is field measured.

	FDC			FDC	
Attribute	<33% (%)	>66% (%)	Attribute	<33% (%)	>66% (%)
DO	35	34	NO_3	43	28
Alkalinity	38	28	Cl	40	31
pH	37	33	HCO_3	39	30
Temperature	41	29	SO_4	41	30
DIC	0	83	Ca	40	31
DOC	48	25	K	40	31
TOC	38	36	Mg	40	30
DON	46	27	Na	40	31
TON	42	30	Si	42	29
TDN	49	26	Al	51	22

Over 25% of all samples are collected at low flow (>66% tercile) for all solutes (except Al) and HCO_3 is exclusively sampled at low and moderate flows.

3.4 Coincidence of Sampling Across Species

A key strength of the USGS sampling program is that a large number of water constituents are measured simultaneously, which allows concentration ratios and mixing models to be more readily developed (Godsey et al. 2019). We report this information as a table of fractions of coincident samples (Table 3). For example, we see that daily discharge is co-sampled with the water chemistry constituents >90% of the time (right most column), however only about 10-30% of discharge sampling dates have a water chemistry measurement (bottom most row). Lithogenic solutes and some anions appear to be co-sampled over 90% of the time, while many of the biological solutes were sampled less often. In this case, between 30%-80% of samples had

coincident ion chemistry, with constituents like DOC and NO_3 being more likely to have coincident ion chemistry than TN, TON, DON, and DO. The nitrogen sampling was often coincident between TN and NO_3, with the other nitrogen species sampled less coincidentally.

3.4 Coincidence of Sampling Across Species

Another key strength of the USGS sampling program is that a large number of water constituents are measured simultaneously, which allows concentration ratios and mixing models to be more readily developed (Godsey et al.,). We report this information as a table of fractions of coincident samples (Table X) from both datasets. For example, we see that daily discharge is co-sampled with the water chemistry constituents >90% of the time (right most column), however only about 10-30% of discharge sampling dates have a water chemistry measurement (bottom most row). Likely because of similar analytical ion chemical analysis, the base cation and some anions appear to be co-sampled >90%, including Ca, SO4, Mg, Na, Si, and K. Many of the biological solutes were sampled less often and only 30%-80% of samples had coincident ion chemistry, with constituents like DOC and NO3 being more likely to have coincident ion chemistry than TN, TON, DON, and DO. The nitrogen sampling was often coincident between TN and NO3, with the other nitrogen species sampled less coincidentally. We leverage this coincidence sampling of ion chemistry to investigate weathering relationships in Section 4.

Table from Dustin

Table 3: Percent of samples stream water chemistry datasets in CAMELS-Chem for all constituents. Table is read as the percent of co-sampling with column constituent in all samples in the top right of table and the row constituent in the bottom left of table. For example, 95% of Temperature (Temp) have discharge (Q) samples and 88% of Q samples have Temp samples. DO=dissolved Oxygen, TDN=total dissolved nitrogen, DOC=dissolved organic carbon, TOC=total organic carbon, *Alk=alkalinity, DON=dissolved organic nitrogen. See table 1 for USGS parameter codes for most solutes. *USGS parameter codes for alkalinity (not included in table 1) = 418,421,99431, and 99432.

	Temp	Q	DO	Cl	Na	K	Mg	Si	Al	N	TDN	NO₃	SO₄	Ca	DOC	TOC	pH	Alk	HCO₃	DON
Temp	100	95	37	31	28	28	29	26	9	14	7	18	30	29	13	7	28	1	6	6
Q	88	100	33	30	26	26	27	24	9	13	7	18	28	27	14	6	26	1	6	5
DO	96	92	100	52	49	48	51	42	14	32	11	30	50	51	14	17	48	1	16	13
Cl	86	91	56	100	83	83	85	75	24	24	15	43	88	85	38	11	74	2	17	10
Na	89	90	59	93	100	97	100	86	27	26	16	43	93	99	40	11	79	2	17	11
K	90	90	60	94	100	100	100	86	27	26	16	44	95	99	40	11	79	2	17	11
Mg	89	90	60	92	96	94	100	83	28	25	16	42	91	99	39	12	79	2	16	11
Si	87	90	55	92	93	91	93	100	27	28	20	48	91	93	45	14	81	2	19	16
Al	89	96	54	88	87	86	93	80	100	24	23	58	84	93	44	8	90	2	17	6

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N	91	91	80	56	54	53	54	53	16	100	25	36	54	54	13	27	52	1	15	33
TDN	93	96	56	69	67	67	67	77	29	50	100	70	68	67	52	28	69	0	14	54
NO₃	88	95	58	76	67	67	68	69	28	27	26	100	74	68	50	12	65	1	21	16
SO₄	90	90	58	95	90	89	91	81	25	25	16	46	100	90	41	11	77	2	18	11
Ca	89	90	60	92	96	94	100	83	28	25	16	42	91	100	39	12	79	2	16	11
DOC	85	98	35	89	82	82	83	87	29	13	26	66	89	83	100	7	73	1	17	14
TOC	93	81	82	47	44	43	47	51	10	51	26	31	43	47	13	100	61	0	9	26
pH	90	91	59	85	81	79	84	77	29	26	17	43	82	83	36	16	100	2	16	10
Alk	97	98	96	96	92	91	94	92	31	29	6	53	92	94	39	1	94	100	97	2
HCO₃	93	96	93	87	78	78	78	80	25	34	16	63	86	78	38	10	72	8	100	14
DON	91	95	79	58	57	57	57	74	9	80	67	51	56	57	35	35	52	0	15	100

3.5. Atmospheric deposition data

Wet deposition data were obtained from NADP for the earliest availability, which started in 1985 and ended (at the time of publication) in 2018. The data product is generally an inverse distance weighted interpolation of the wet deposition observation stations and reported as a concentration and deposition (mass per area); more details are provided on their website. Data rasters were positioned to correspond to CAMELS catchment shape files to determine total watershed deposition for 10 species for a given year (Figure 7). Quantum GIS 3.12 was used to calculate mean, minimum, maximum, and standard deviation of the concentration and deposition values for each catchment and each year (Table 4).

Table 4: NADP depositional dataset, attribute, name, concentration and deposition units.

Attribute	Name	Concentration units	Deposition units

H$^+$	Hydrogen	mg/l	kg/ha
NH$_4$	Ammonium	mg/l	kg/ha
NO$_3$	Nitrate	mg/l	kg/ha
NO$_3$ + NH$_4$	Inorganic Nitrogen	mg/l N	kg/ha
Cl	Chloride	ug/l	kg/ha
SO$_4$	Sulfate	mg/l	kg/ha
Ca	Calcium	mg/l	kg/ha
K	Potassium	mg/l	kg/ha
Mg	Magnesium	mg/l	kg/ha
Na	Sodium	mg/l	kg/ha

Atmospheric deposition needs to be considered when evaluating water chemistry patterns and especially for weathering studies, the contribution of atmospheric deposition needs to be corrected for (Berner and Berner 2012). For example, Cl and Na deposition values are higher in coastal areas (Figure 7e and j), while NH$_4$ and NO$_3$ deposition vales are higher in places where anthropogenic inputs of fertilizer are high (Figure 7b and c). Ca typically has higher values away from coastal areas and is strongly impacted by local bedrock and soil composition (Berner and Berner 2012). In many cases these patterns are consistent with patterns in stream chemistry (e.g. Figure 1j for stream NO$_3$).

Wet deposition can help explain some context for water chemistry patterns. For example, Cl deposition (Figure 43b) is higher streamflow Cl concentrations along the coast relative to more inland catchment (Figure 3). Conversely, atmospheric deposition of NO3 is much higher in the Midwest and other places where anthropogenic inputs of fertilizer are high (Figure 4a) and are consistent with patterns in stream chemistry (Figure 32e). The annual resolution of the wet deposition data is sufficient to investigate trends in air and water quality (see example 4.3) and could be supplemented as additional datasets become available (i.e., total wet and dry deposition; Schwede et al., 2014).We explore how the consistency of spatial and temporal sampling can affect analysis techniques and inferences in Section 4.

4 Example Analyses Using CAMELS-Chem

To motivate adoption of this dataset by the larger scientific community, especially in fields that span multiple disciplines, we intentionally decided to offer We illustrate the research potential of CAMELS-Chem using three themes and examples in three themes: 1. by investigating trends in SO$_4$SO4 deposition and stream chemistry over the continental U.S we show highlight atmospheric-aquatic linkages, 2. by investigating continental-scale C-Q relations we highlight hydrological and biogeochemical linkages, and 3. by investigating weathering patterns we highlight geological-biogeochemical linkages. Our

goal for this section is to demonstrate the unique value of the CAMEL-Chem dataset, its potential limitations, and to motivate future work.

4.1 Trends in Atmospheric SO_4~~SO4~~ Deposition and Stream Chemistry

4.1.1 Background and Motivation

The Industrial Revolution caused a rapid increase in fossil fuel emissions, which introduced acid anions (SO_4, NO_3~~NO3~~) in excess of background conditions leading to acidic precipitation throughout many industrialized regions (Newell & Skjelkvåle, 1997). The Clean Air Act in 1970 and subsequent amendment in 1990 led to major reduction in air pollution as apparent in progressively decreasing deposition amounts (~~Accessed September 20, 2020: https://www.epa.gov/air-trends/sulfur-dioxide-trends~~). These significant changes in atmospheric composition served as an experiment in stream chemistry response (Stoddard et al, 1990) and motivated several studies across the US and Europe. For example, Stoddard et al. (1990) showed that stream water acid anion concentration declined more in the 1990s than the 1980s and later research indicated that effects were larger in Europe than North America (Garmo et al., 2014). In the Northeastern U.S., SO_4~~SO4~~ stream chemistry has generally responded to declines in SO_4~~SO4~~ deposition (McHale et al., 2017; Siemion et al., 2018). However, catchment properties and flow regime were shown to impact the sensitivity of stream response to shifts in deposition (Clow et al., 2018; Murdoch et al., 2006). The lack of co-located long-term deposition data, stream water chemistry and discharge data, and catchment attributes hinders investigation of the legacy of effects of acid rain on stream chemistry at continental scales.

4.1.2 Analysis and Findings

CAMELS-Chem provides new potential to analyze the effects of acid deposition on long-term stream chemistry trends across a range of hydrological conditions. Many (but not all) sites have >100 SO_4 stream samples spanning over 20 years of record (Figure 2m). Our analyses of FDC show that bias towards part of the flow regime when SO_4 samples are common and depend on the location of interest (Figure 3l). To investigate trends in atmospheric SO_4 deposition and resulting trends in stream water chemistry, we performed a Mann-Kendall test for three timeframes (Hirsch and Slack 1984). Our results are in agreement with previous findings of declining SO_4 deposition following the 1990 Clear Air Amendments (Figure 7, Garmo et al. (2014)). As expected, plotting trends in SO_4 stream chemistry and wet deposition for an earlier timeframe (1985-1992, Figure 8a) decreasing trends in SO_4 deposition and corresponding decreasing trends in SO_4 stream chemistry are apparent. Wet deposition trends remain decreasing in the following two decades (1992-2002 and 2002-2010), but without much response in SO_4 stream chemistry. This initial analysis provides a starting point for hypothesis testing - for example, on the role of catchment attributes such as the dominant geology (Figure 8a-c). Furthermore, we hope to motivate more sophisticated statistical and machine learning techniques to investigate coupled trends in solutes and the role of climate physiographic information as predictor variables.

4.2 Weathering Response

4.2.1 Background and Motivation

Weathering (i.e. the breakdown of bedrock and regolith) involves key physical and chemical processes that shape Earth surface processes and provides important nutrients for all ecosystems. Further, weathering of silicate minerals regulates global atmospheric CO_2 levels over geologic time scales (Spence and Telmer 2005), and weathering of carbonate rocks modulate CO_2 levels at the human to century time scales (Ulloa-Cedamanos et al. 2021). Riverine composition is often used as an indicator for weathering rates and to draw conclusions on implications at larger scales. A classic example is the study by Gaillardet et al. (1999) where 60 of the world largest rivers were used to show a strong role of bedrock lithology on weathering rates from Si effluxes. To display the impact of major rock classes (i.e. silicates, carbonates, evaporites) on riverine composition, the use of molar ratios for geogenic species (Ca/Na, Mg/Na, HCO_3/Na) instead of absolute concentrations is useful, because large differences in concentrations between solid and liquid phases make comparisons difficult. CAMELS-Chem provides complete and co-sampled water chemistry datasets, with known lithology, making these types of weathering analyses possible across CONUS.

4.2.2 Analysis and Findings

We display these molar ratios of stream water composition for all CAMELS-Chem sites (with a sample number larger than 5) as a function of bedrock lithology including igneous, metamorphic and sedimentary rocks (Figure 9). We included only samples in the lower tercile of daily discharge values because the low flow discharge is more likely from longer residence groundwater that carries the weathering signal. The lower tercile encompasses more Ca and Mg samples than HCO_3 and Na samples based on overall sampling frequency (Figure 3m and o vs. Figure 3k and p, respectively). Similar to previous studies (Gaillardet et al. 1999), we observe a pattern based on lithology, with catchments underlain by carbonate plotting in the upper right (i.e., high Ca/Na, Mg/Na, and HCO_3/Na ratios) and unconsolidated sediments plotting in the lower left (e.g., low Ca/Na, Mg/Na, and HCO_3/Na ratios). These results are consistent with the high weathering rates of carbonates, where even small amounts of carbonate lithology lead to significant shifts to higher Ca/Na (calcite endmember) and Mg/Na (presence of dolomite) ratios. Although beyond the scope of this work, CAMELS-Chem gives sufficient samples to provide uncertainty estimates in Figure 9, particularly given the uneven number of samples and distribution across solutes (Figure 1). Including baseflow index further reveals higher baseflow in carbonates-underlain catchments (Figure 9), which is consistent with fractures and highly conductive conduits that are common in carbonate aquifers (Hartmann et al. 2009). In contrast, unconsolidated sediments tend to have low weathering rates and low baseflow index (Figure 9).

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4.2 Concentration-Discharge Relationships

4.2.1 Background and Motivation

Concentration-discharge (C-Q) relationships are routinely used to compute solute loads for mass budgets (Cohn et al., 1989) and have been used to infer catchment effects on biogeochemical cycling (Basu et al., 2010, Musolff et al., 2015). When event-scale data is not available, routine sampling can be used to compute a log-log C-Q relationship to visualize the extent of discharge dependency. The log-log C-Q relationship is considered chemostatic if the regression slope is near zero, implying that export of that solute is negligibly influenced by discharge (Godsey et al., 2009, Underwood et al., 2017, Zhi and Li, 2020).

This chemostatic relation is more likely for geogenic solutes, like Si and Ca, and less so for biogenic solutes, like nutrients, with large anthropogenic or natural legacy effects (Musolff et al., 2015). Recent work by Godsey et al., (2019) suggests that groundwater and fast chemical reactions buffer C-Q relationships towards chemostasis, but that the baseline concentrations reflect catchment differences in geology, land use, etc. Godsey et al. (2019) also found that nutrients can be chemostatic, but their long-term mean concentrations correlated more to land use than climate. Moreover, sampling bias occurring at high and low streamflow (Figure 5, as well as rising and falling limb of hydrograph, season, etc.) may bias effects towards chemostatic behavior (Zhi et al., 2019). These efforts with CAMELS-Chem show the value of large-sample datasets for inferring C-Q relations and their uncertainty.

4.2.2 Analysis and Findings

The CAMELS-Chem dataset offers potential to resolve C-Q relationships by improving discharge estimates and pairing with substantial existing physiographic information. Here we repeat the methods and analysis of Godsey et al. (2019) to show similar event-scale (i.e. instananeous water chemistry and discharge) C-Q slopes across the overlapping solutes (Figure 6). The existing physiographic data compiled by (Addor et al., 2017) allows us to easily filter by the aridity index to match the previous analysis of Godsey et al. 2019. Arid catchments were defined as those in which potential evapotranspiration was greater than actual evapotranspiration, the reverse was used to determine humid catchments. In general, the findings for CONUS sites are consistent with the global-scale analysis of Godsey et al. (2019), showing near-chemostatic behavior of DOC and Si. In contrast to Godsey et al. (2019), Na for the CAMELS sites shows more pronounced negative slopes in arid catchments than in humid catchments. This analysis could be expanded to include additional solutes, or physiographic data, in more complex statistical or machine learning based approaches that attempt to infer association with biogeochemical process and uncertainty due to irregular and limited sampling.

The CAMELS-Chem dataset has several advantages in this C-Q analysis: 1) instantaneous (hourly) discharge data were used to supplement the NWIS database and 2) 30-year daily discharge records are a reference for C-Q ranges. Because Q values are more likely to change over daily periods at high flows than low flows, instantaneous discharge measurements are more critical

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on high flow days than low flow days. Instantaneous discharge during the chemistry sampling can be > 50% higher or lower than the daily mean discharge for a range of important solutes, despite little overall bias (Figure S4). Thus, the CAMELS-Chem discharge data could improve accuracy in previous C-Q analysis that rely on daily measured or modeled discharge data. The 30-year daily discharge records can be used to assess the degree of discharge variation covered by chemistry sampling dates. We show this as the percent of the long-term FDC covered by the minimum and maximum discharge during sampling in Figure 7. While many sites cover > 90% of the FDC, like those in the upper Midwest, other locations cover less than 50% of the FDC, like many of the Gulf Coast sites. The slope of the response of the concentration discharge relationship can be different at high and low flows (Li et al., 2020). The diverse number of samples with uneven collection dates, as well as the lack of discharge variation during solute sampling, suggest that future work should explore C-Q uncertainty estimates using more sophisticated statistical techniques with CAMELS-Chem.

5 Summary and Conclusions

We developed and released CAMELS-Chem, a relational database comprising water chemistry measurements, corresponding instantaneous discharge, and wet deposition data. As a relational database, this provides fast query processing, enforces data integrity, provides detailed information about current data and schema (i.e., relational structure), and represents a flexible platform to export data in a consistent format for external analysis. This database is continuously updated, and collaborations are welcome to explore the full capacity of the database. However, the accompanying dataset available on Hydroshare and codes on GitHub will be sufficient for most applications.

This dataset has several advantages because it is paired with hydrometeorological and hydrological modelling data (Newman et al. 2015), as well as catchment physiographic properties (Addor et al. 2017). In addition, the consistency of U.S. Geological Survey (USGS) water chemistry analysis increases the comparability of the dataset across regions and decades, which is a well-recognized problem (Niu et al. 2014, Godsey et al. 2019). The connection between catchment attributes, long-term discharge and stream chemistry data as well as paired atmospheric deposition data allows for novel ways of data-driven investigation of integrated Earth science studies. The use of CAMELS-Chem in 'big data' applications of advanced statistical or machine learning tools holds much promise in this regard. For example, large data approaches can develop new predictive tools for ungauged locations to help with water quality management (Zhi et al. 2020) or make process inferences and improve predictive models (Nearing et al. 2021). All of the research directions take advantage of the many unique aspects of CAMELS-Chem, which bodes well for its adoption and use by a variety of scientific disciplines.

However, the user needs to take the limitations of these data into account: for example, the sampling frequency and chemical variables of interest are not consistent over time, reflecting changing priorities and budgets within the USGS. This may require

sub-setting data into the catchments with longer records or using new machine learning and statistical techniques that can take advantage of sparse data within a larger data analysis.

Code and Data Availability

The dataset is available on Hydroshare link https://www.hydroshare.org/resource/841f5e85085c423f889ac809c1bed4ac/. All code used for figures will be made available GitHub after the review process is completed.

Author Contributions

G.S., A.H., and J.P. conceived and planned the study. G.S., T.A., D.K., H.M. and K.U. contributed to the analysis. L.L, J.P., T.A., D.R. contributed to the case studies, G.S. and I.U. curated the database. All authors contributed to the writing of the paper.

Competing Interests

(a) Discharge (*n* = 509)

Mean level (cfs)
○ 1700 ○ 3400 ○ 8600 ○ 14000
Coefficient of variation (%)
<25 50 75 100 >100

(b) DO (*n* = 381)

Mean conc. (mg/l)
○ 2.5 ○ 6.4 ○ 10.0
Coefficient of variation (%)
<25 50 75 100

(c) pH (*n* = 420)

Mean level (std units)
○ 5.4 ○ 8.7
Coefficient of variation (%)
<25 50 75

(d) Temperature (*n* = 515)

Mean temp. (°C)
○ 5.5 ○ 14.0 ○ 22.0
Coefficient of variation (%)
<25 50 75 100 >100

(e) DOC (*n* = 179)

Mean conc. (mg/l)
○ 4.2 ○ 8.3 ○ 21.0 ○ 33.0
Coefficient of variation (%)
<25 50 75 100 >100

(f) TOC (*n* = 165)

Mean conc. (mg/l)
○ 5.0 ○ 9.9 ○ 25.0 ○ 40.0
Coefficient of variation (%)
<25 50 75 100 >100

(g) DON (*n* = 183)

Mean conc. (mg/l)
○ 0.16 ○ 0.32 ○ 0.80 ○ 1.30
Coefficient of variation (%)
<25 50 75 100 >100

(h) TON (*n* = 258)

Mean conc. (mg/l)
○ 0.79 ○ 1.60 ○ 3.90 ○ 6.30
Coefficient of variation (%)
<25 50 75 100 >100

(i) TDN (*n* = 178)

Mean conc. (mg/l)
○ 0.81 ○ 1.60 ○ 4.10 ○ 6.50
Coefficient of variation (%)
<25 50 75 100 >100

(j) NO_3 (*n* = 310)

Mean conc. (mg N/l)
○ 0.74 ○ 1.50 ○ 3.70 ○ 5.90
Coefficient of variation (%)
<25 50 75 100 >100

(k) Cl (*n* = 404)

Mean conc. (mg/l)
○ 550 ○ 1100 ○ 2800 ○ 4400
Coefficient of variation (%)
<25 50 75 100 >100

(l) HCO_3 (*n* = 170)

Mean conc. (mg/l)
○ 79 ○ 160 ○ 390 ○ 630
Coefficient of variation (%)
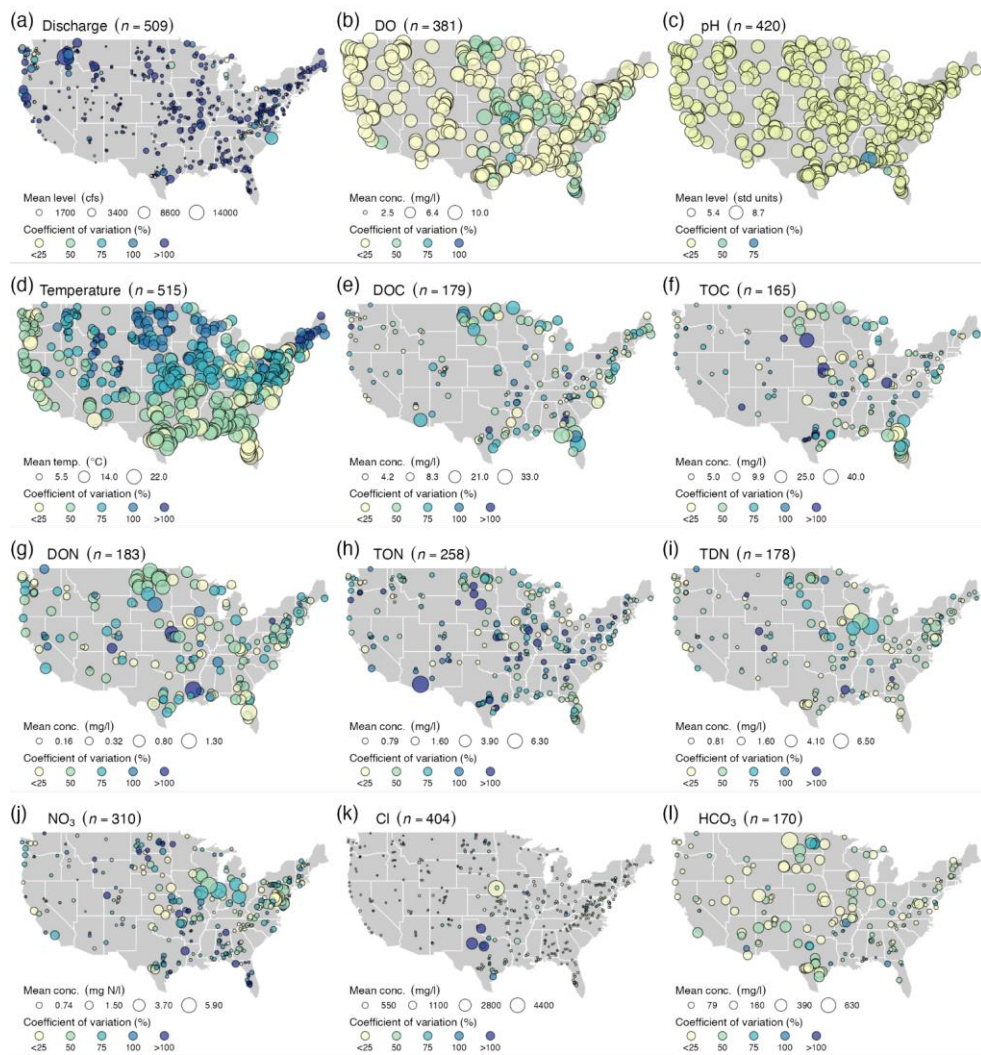<25 50 75 100 >100

Figure 1: The mean concentration (symbol size) and coefficient of variation (in %, symbol color) for the stream data between 1980 and 2018 for (a) discharge, (b) dissolved oxygen (DO), (c) pH (field), (d) temperature, (e) dissolved organic carbon (DOC), (f) total organic carbon (TOC), (g) dissolved organic nitrogen (DON), (h) total organic nitrogen (TON), (i) total dissolved nitrogen (TDN), (j) nitrate (NO_3), (k) Cl, (l) bicarbonate (HCO_3), (m) sulfate (SO_4), (n) Ca, (o) K, (p) Mg, (q) Na, (r) Si, and (s) Al. The inset histogram shows the number of samples by 8-year periods.
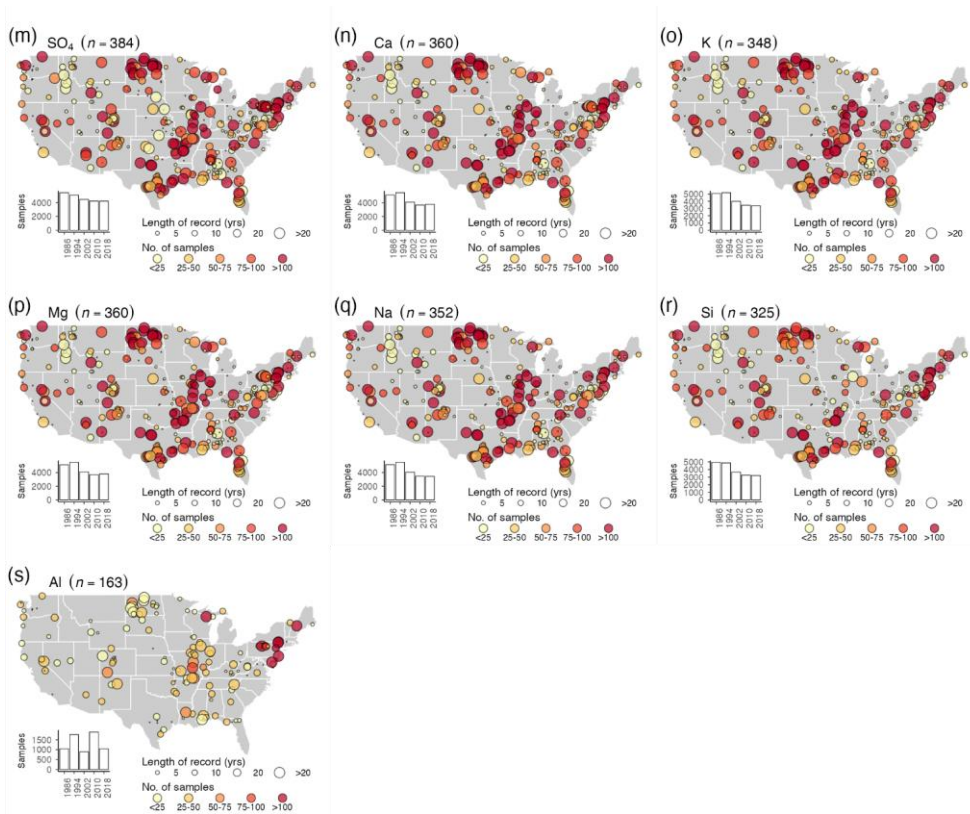
Figure 2: The number of samples (symbol color) and length or record (symbol size) for the stream data between 1980 and 2018 for all flow conditions (a) discharge, (b) dissolved oxygen (DO), (c) pH (field), (d) temperature, (e) dissolved organic carbon (DOC), (f) total organic carbon (TOC), (g) dissolved organic nitrogen (DON), (h) total organic nitrogen (TON), (i) total dissolved nitrogen (TDN), (j) nitrate (NO_3), (k) Cl, (l) bicarbonate (HCO_3), (m) sulfate (SO_4), (n) Ca, (o) K, (p) Mg, (q) Na, (r) Si, and (s) Al. The inset histogram shows the number of samples by 8-year periods.
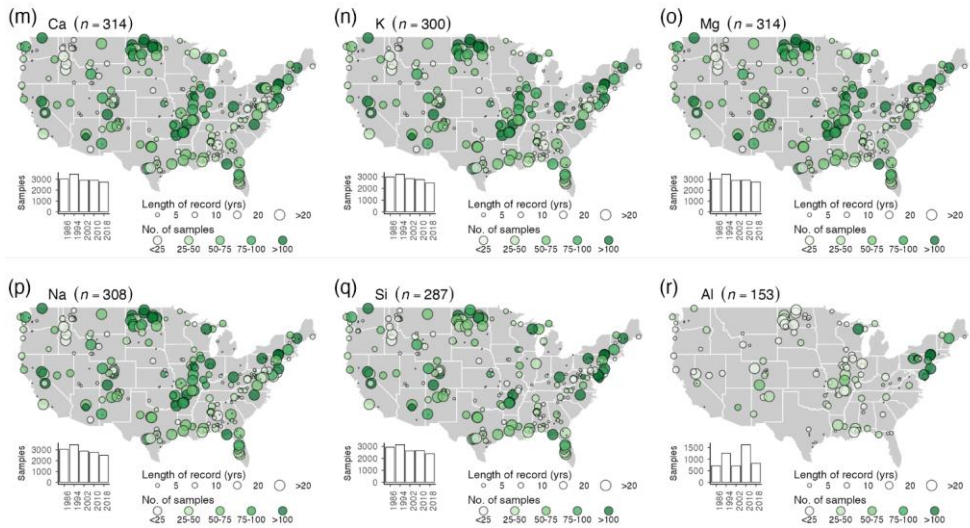
Figure 3: The number of samples (symbol color) and length or record (symbol size) for the stream data at low flows (flow duration curve >66%) between 1980 and 2018 for (a) discharge, (b) dissolved oxygen (DO), (c) pH (field), (d) temperature, (e) dissolved organic carbon (DOC), (f) total organic carbon (TOC), (g) dissolved organic nitrogen (DON), (h) total organic nitrogen (TON), (i) total dissolved nitrogen (TDN), (j) nitrate (NO$_3$), (k) Cl, (l) bicarbonate (HCO$_3$), (m) sulfate (SO$_4$), (n) Ca, (o) K, (p) Mg, (q) Na, (r) Si, and (s) Al. The inset histogram shows the number of samples by 8-year periods.
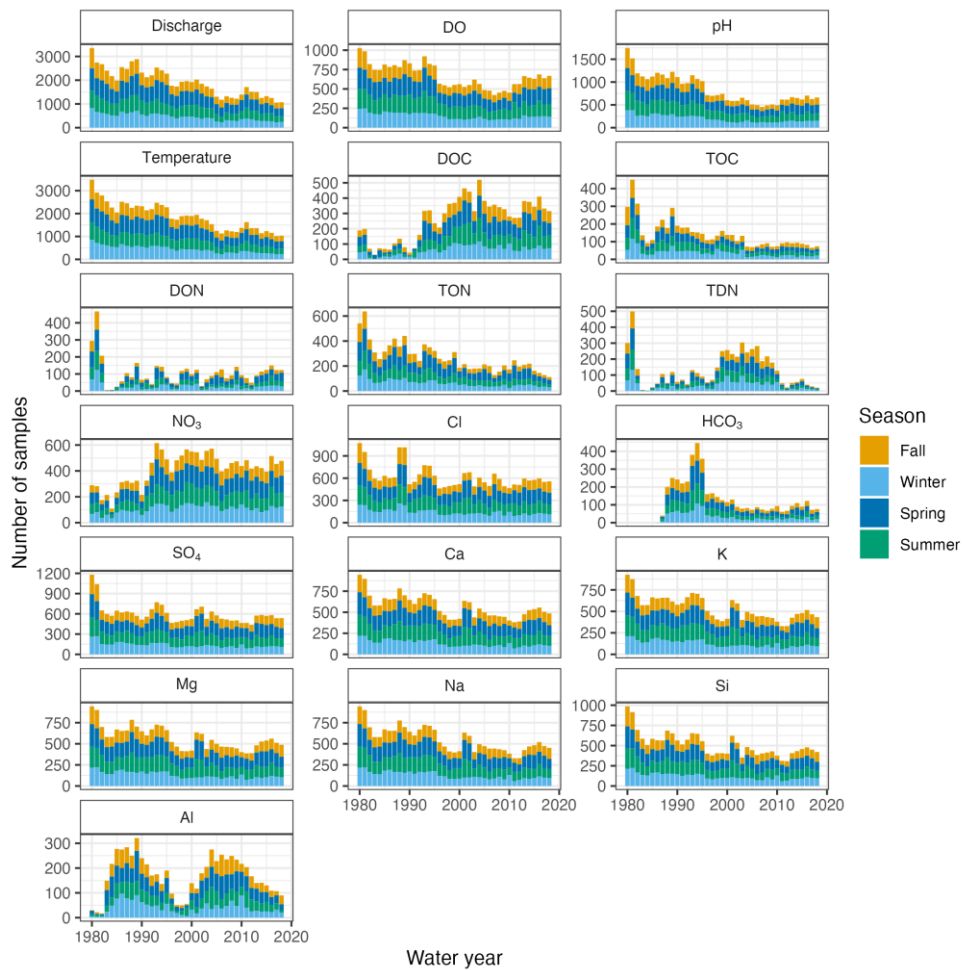
Figure 4: The number of samples by water year and seasons (color code) for the stream data between 1980 and 2018 for discharge, dissolved oxygen (DO), pH (field), temperature, dissolved organic carbon (DOC), total organic carbon (TOC), dissolved organic nitrogen (DON), total organic nitrogen (TON), (i) total dissolved nitrogen (TDN), (j) nitrate (NO_3), (k) Cl, (l) bicarbonate (HCO_3), (m) sulfate (SO_4), (n) Ca, K, Mg, Na, Si, and Al.
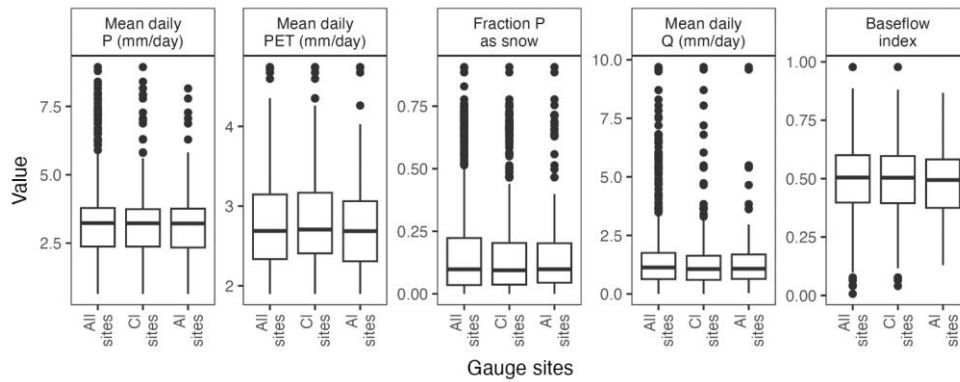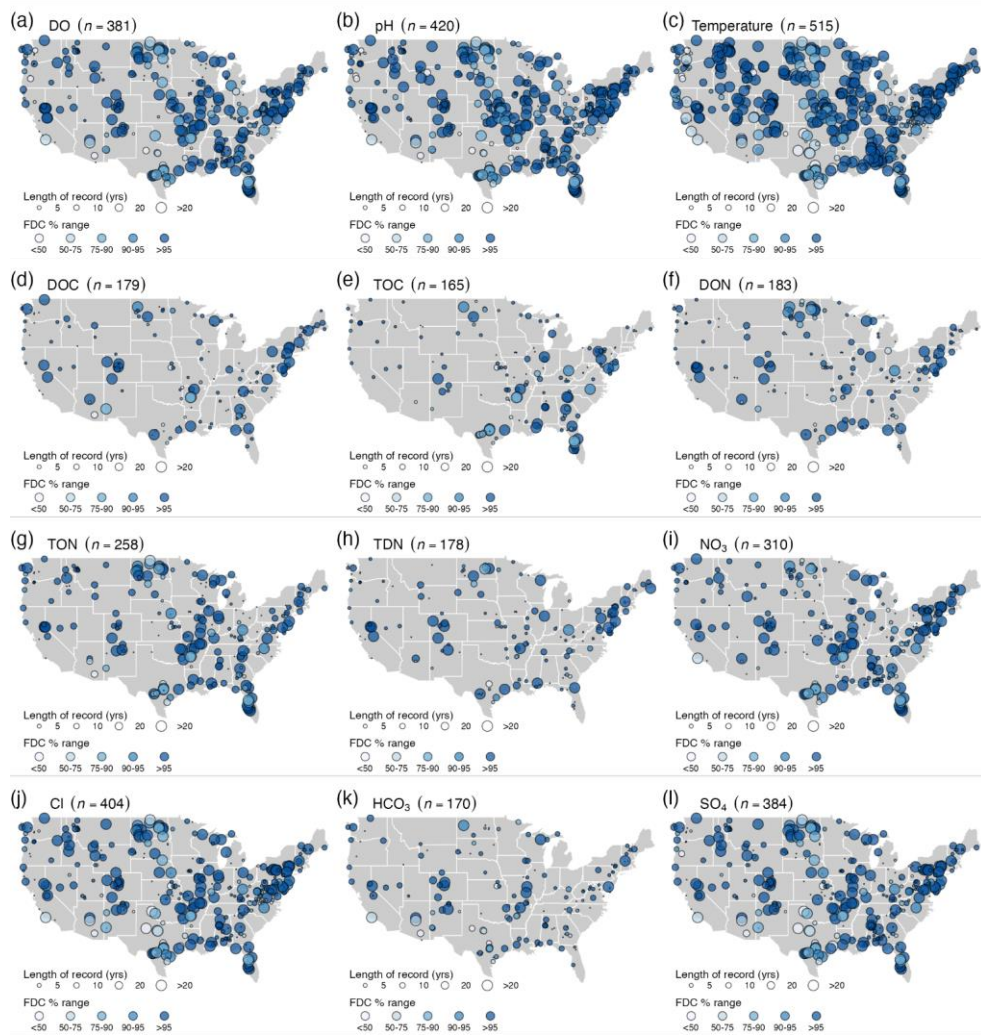
Figure 5. Distribution of values for climate and hydrological metrics for all CAMELS gauges ($n = 671$) versus gauges that have chloride (Cl) data ($n = 404$) or aluminum (Al) data ($n = 263$) when the data are subset for water years 1980 to 2018. P = precipitation. PET = potential evapotranspiration. Q = discharge. Boxplots represent the median and interquartile range with outlier values shown as points. See Addor et al. 2017 for more information on attribute description.
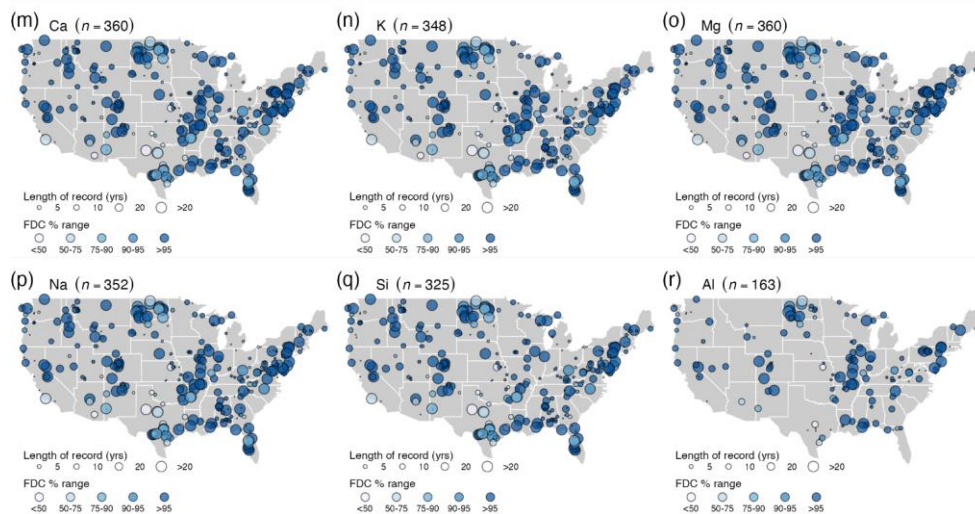
(a) DO (*n* = 381)
Length of record (yrs)
5 10 20 >20
FDC % range
<50 50-75 75-90 90-95 >95

(b) pH (*n* = 420)
Length of record (yrs)
5 10 20 >20
FDC % range
<50 50-75 75-90 90-95 >95

(c) Temperature (*n* = 515)
Length of record (yrs)
5 10 20 >20
FDC % range
<50 50-75 75-90 90-95 >95

(d) DOC (*n* = 179)
Length of record (yrs)
5 10 20 >20
FDC % range
<50 50-75 75-90 90-95 >95

(e) TOC (*n* = 165)
Length of record (yrs)
5 10 20 >20
FDC % range
<50 50-75 75-90 90-95 >95

(f) DON (*n* = 183)
Length of record (yrs)
5 10 20 >20
FDC % range
<50 50-75 75-90 90-95 >95

(g) TON (*n* = 258)
Length of record (yrs)
5 10 20 >20
FDC % range
<50 50-75 75-90 90-95 >95

(h) TDN (*n* = 178)
Length of record (yrs)
5 10 20 >20
FDC % range
<50 50-75 75-90 90-95 >95

(i) NO_3 (*n* = 310)
Length of record (yrs)
5 10 20 >20
FDC % range
<50 50-75 75-90 90-95 >95

(j) Cl (*n* = 404)
Length of record (yrs)
5 10 20 >20
FDC % range
<50 50-75 75-90 90-95 >95

(k) HCO_3 (*n* = 170)
Length of record (yrs)
5 10 20 >20
FDC % range
<50 50-75 75-90 90-95 >95

(l) SO_4 (*n* = 384)
Length of record (yrs)
5 10 20 >20
FDC % range
<50 50-75 75-90 90-95 >95

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Figure 6: Range of the flow duration curve (FDC %, symbol color) and length or record (symbol size) for the stream data between 1980 and 2018 for (a) discharge, (b) dissolved oxygen (DO), (c) pH (field), (d) temperature, (e) dissolved organic carbon (DOC), (f) total organic carbon (TOC), (g) dissolved organic nitrogen (DON), (h) total organic nitrogen (TON), (i) total dissolved nitrogen (TDN), (j) nitrate (NO_3), (k) Cl, (l) bicarbonate (HCO_3), (m) sulfate (SO_4), (n) Ca, (o) K, (p) Mg, (q) Na, (r) Si, and (s) Al. The inset histogram shows the number of samples by 8-year periods.
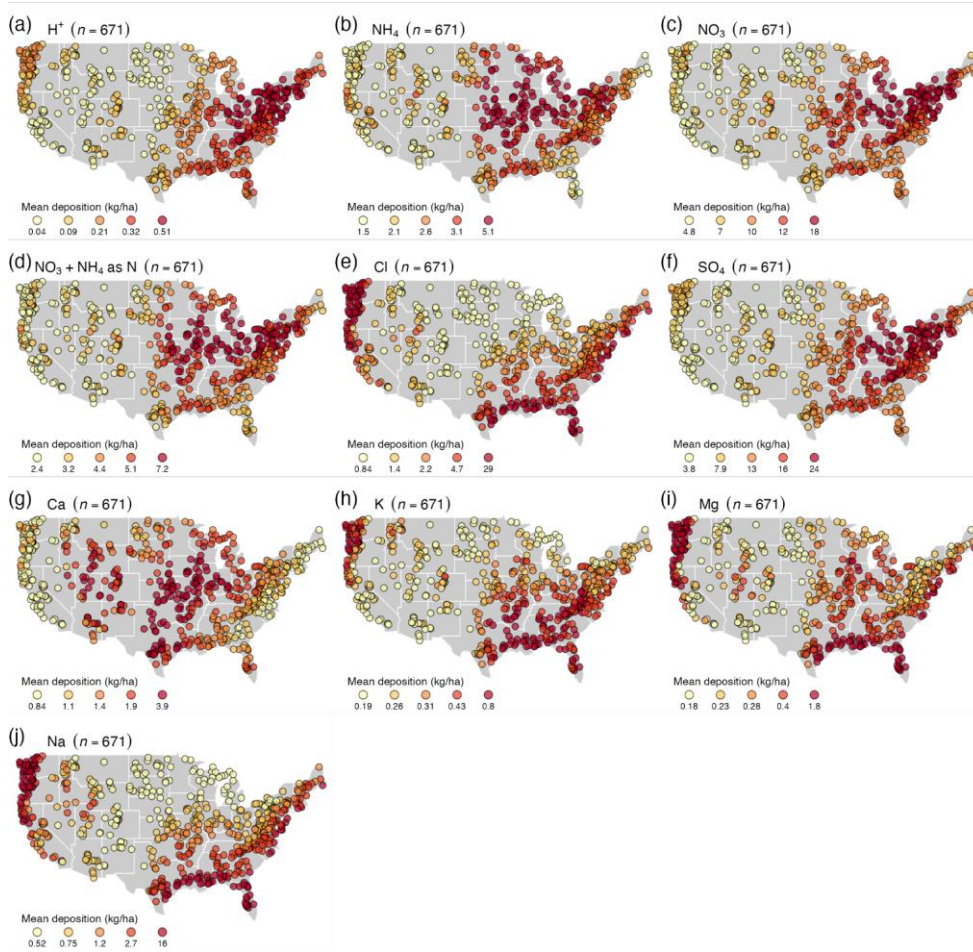
Figure 7: Average atmospheric wet deposition in kg/ha (color code) using data from the NADP network from 1985-2018 for (a) protons (H+), (b) ammonium (NH₄), (c) nitrate (NH₄), (d) inorganic nitrogen (NH₄ and NH₄), (e) Cl, (f) sulfate (SO₄), (g) Ca, (h) K, (i) Mg, and (j) Na. The number of locations represented are referenced as n.
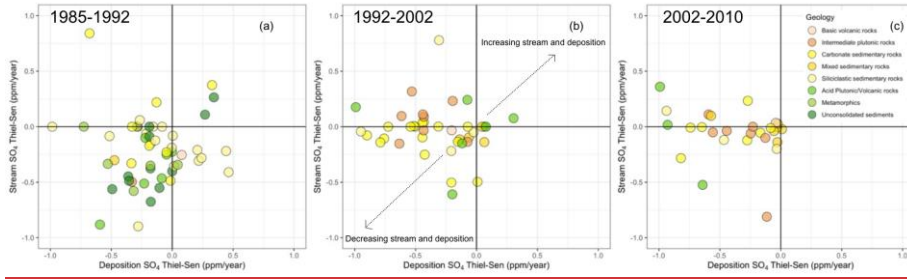
Figure 8: Long-term Sen slope (e.g. average trend) from Mann Kendall analysis of SO_4 deposition (a) from 1985-1992, (b) 1992-2002, and (c) 2002-2010. Symbol color shows dominant geology.
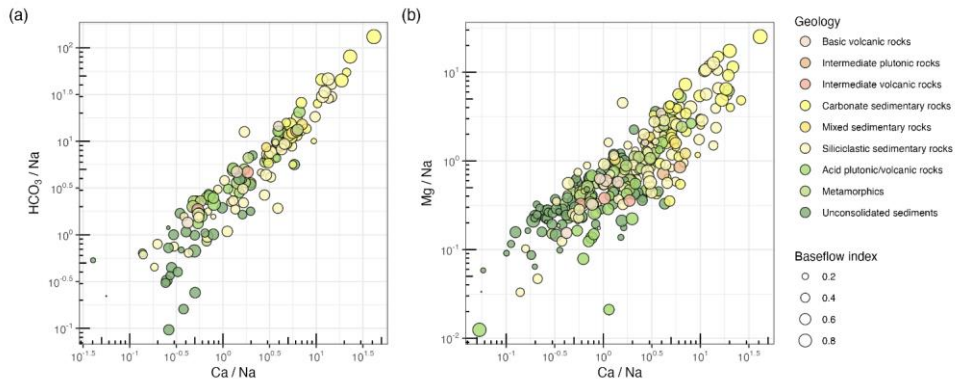
Figure 9: Molar ratios of HCO$_3$ and Mg to Na as a function of the molar ratio of Mg/Na at low flows (flow duration curve >66%). Symbol color is the dominant geology and symbol size is the baseflow index.

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